

Redox Potentials of M(VI)/M(V) Limiting Carbonate Complexes (M = U or Pu) at Different Ionic Strengths and Temperatures Entropy and Heat Capacity.

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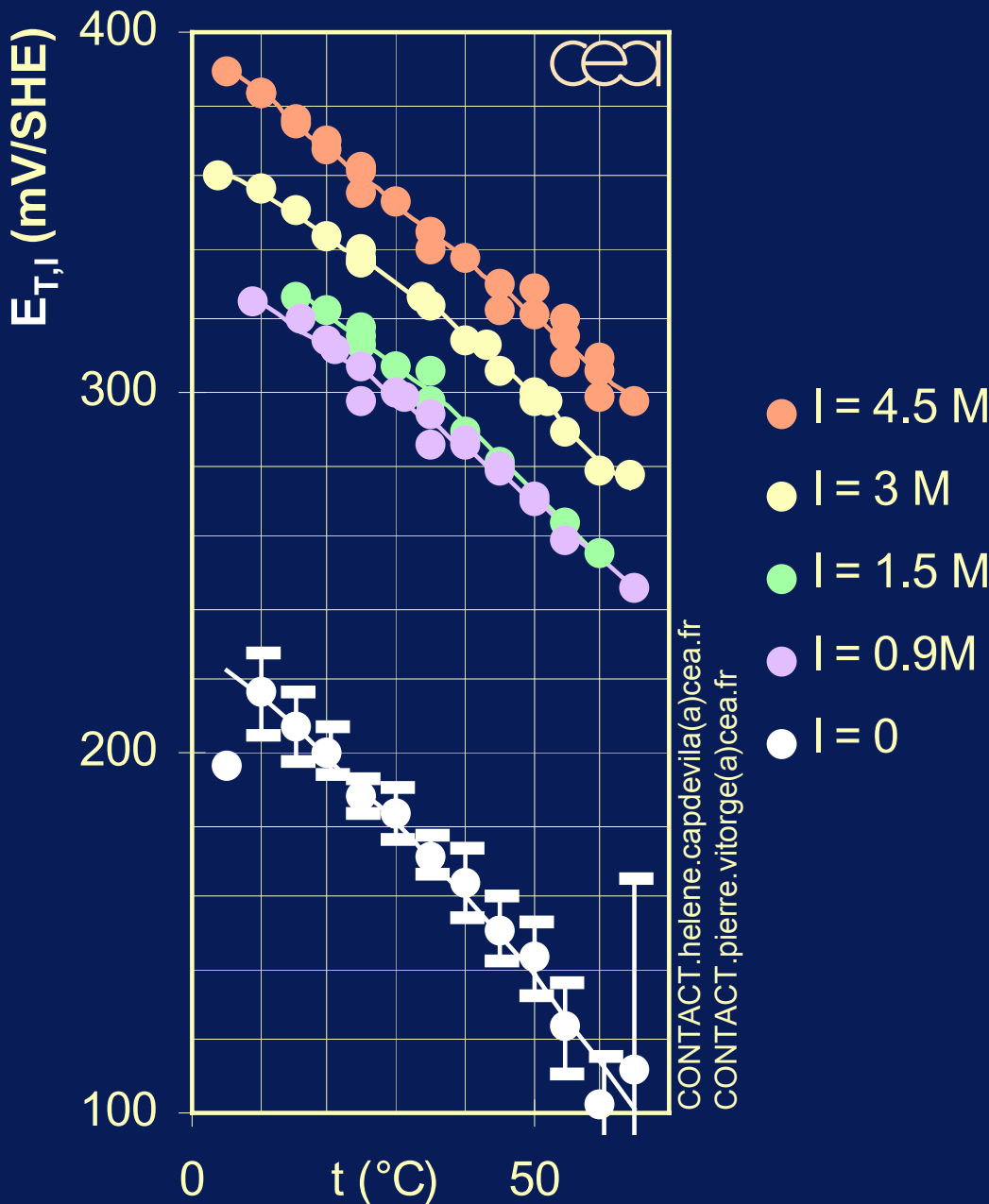
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Temperature Influence on the Formal Potential of the $\text{PuO}_2(\text{CO}_3)_3^{4-}/\text{PuO}_2(\text{CO}_3)_3^{5-}$ Redox Couple



$$E_{T,I} \approx E_{T^0,I} + \frac{\Delta S_{T^0,I}}{F} \Delta T + \frac{\Delta C_{p,T^0,I}}{(2 F T^0)} \Delta T^2$$

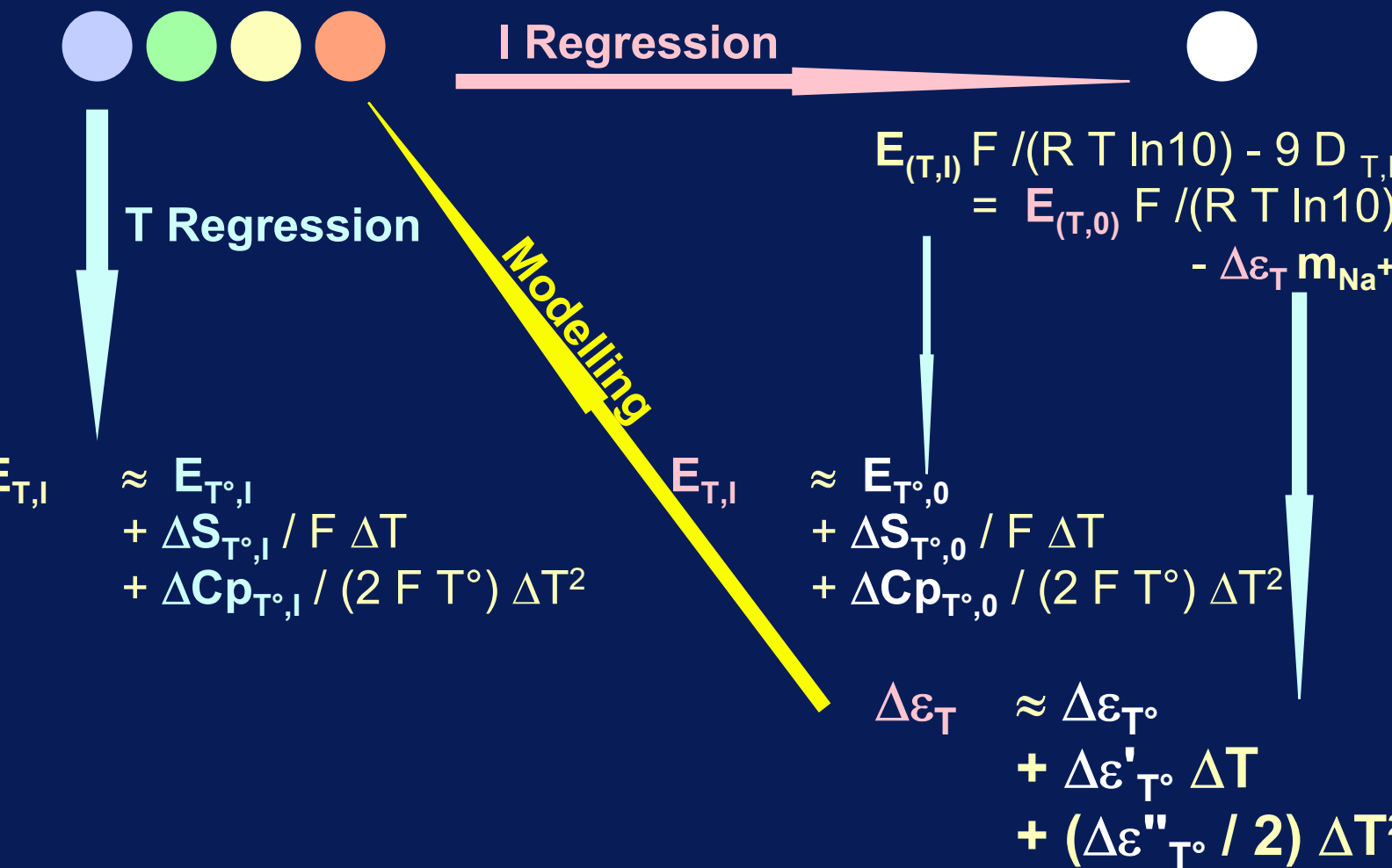
Results (fitted parameters):

Na_2CO_3 (mol.l^{-1})	$E_{T^0,I}$ (mV/SHE)	$\frac{\Delta S_{T^0,I}}{F}$ (mV.K^{-1})	$\frac{\Delta C_{p,T^0,I}}{(2 F T^0)}$ ($\mu\text{V.K}^{-2}$)
0	191 (8)	-1.84 (0.19)	-9.0 (6.5)
0.3	306 (3)	-1.34 (0.09)	-3.8 (3.2)
0.5	315 (3)	-1.47 (0.13)	-7.7 (4.7)
1	338 (2)	-1.30 (0.04)	-8.7 (1.4)
1.5	360 (4)	-1.53 (0.07)	-6.4 (2.7)

Data Treatment

$E_{T,I}$ Experimental Data

Data at $I = 0$



SIT formula for I corrections on E, ΔS , ΔCp and ΔH

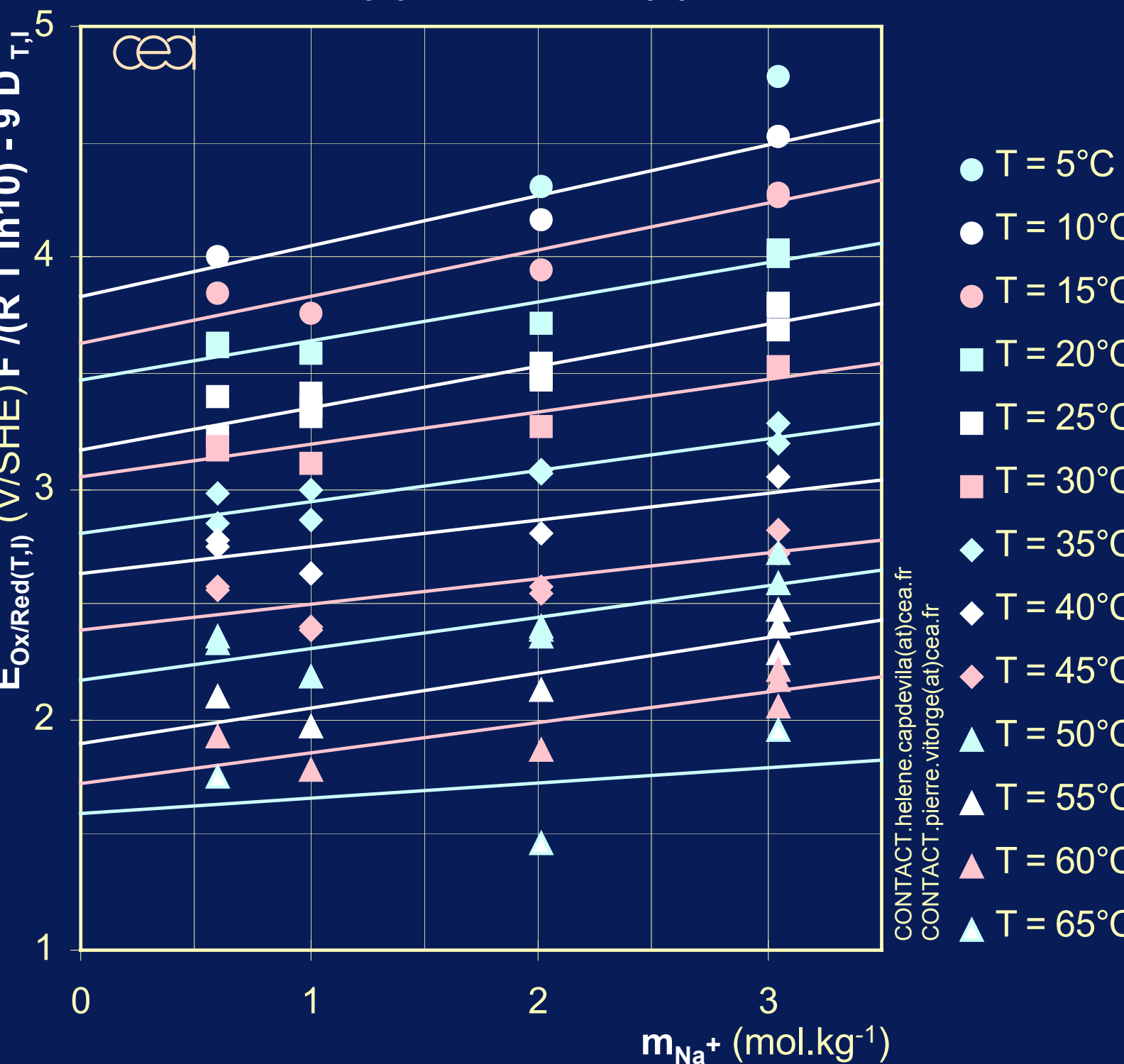
$$E_{(T,I)} = E_{(T,0)} + \left[\frac{9 D_{T,I}}{R T \ln 10} - \Delta \epsilon_T m_{Na^+} \right]$$

$$\Delta S_{T^{\circ},I} = \Delta S_{T^{\circ},0} + \left[\frac{9 (D_{T^{\circ},I} + T^{\circ} D'_{T^{\circ},I})}{R \ln 10} - (\Delta \epsilon_{T^{\circ}} + T^{\circ} \Delta \epsilon'_{T^{\circ}}) m_{Na^+} \right]$$

$$\Delta Cp_{T^{\circ},I} = \Delta Cp_{T^{\circ},0} + \left[\frac{9 (2 D'_{T^{\circ},I} + T^{\circ} D''_{T^{\circ},I})}{R T^{\circ} \ln 10} - (2 \Delta \epsilon'_{T^{\circ}} + T^{\circ} \Delta \epsilon''_{T^{\circ}}) m_{Na^+} \right]$$

$$\Delta H_{T^{\circ},I} = \Delta H_{T^{\circ},0} + \left[\frac{9 D'_{T^{\circ},I}}{R T^{\circ 2} \ln 10} - \Delta \epsilon'_{T^{\circ}} m_{Na^+} \right]$$

Ionic Strength Influence on the Formal Potential of the $\text{PuO}_2(\text{CO}_3)_3^{4-}/\text{PuO}_2(\text{CO}_3)_3^{5-}$ Redox Couple



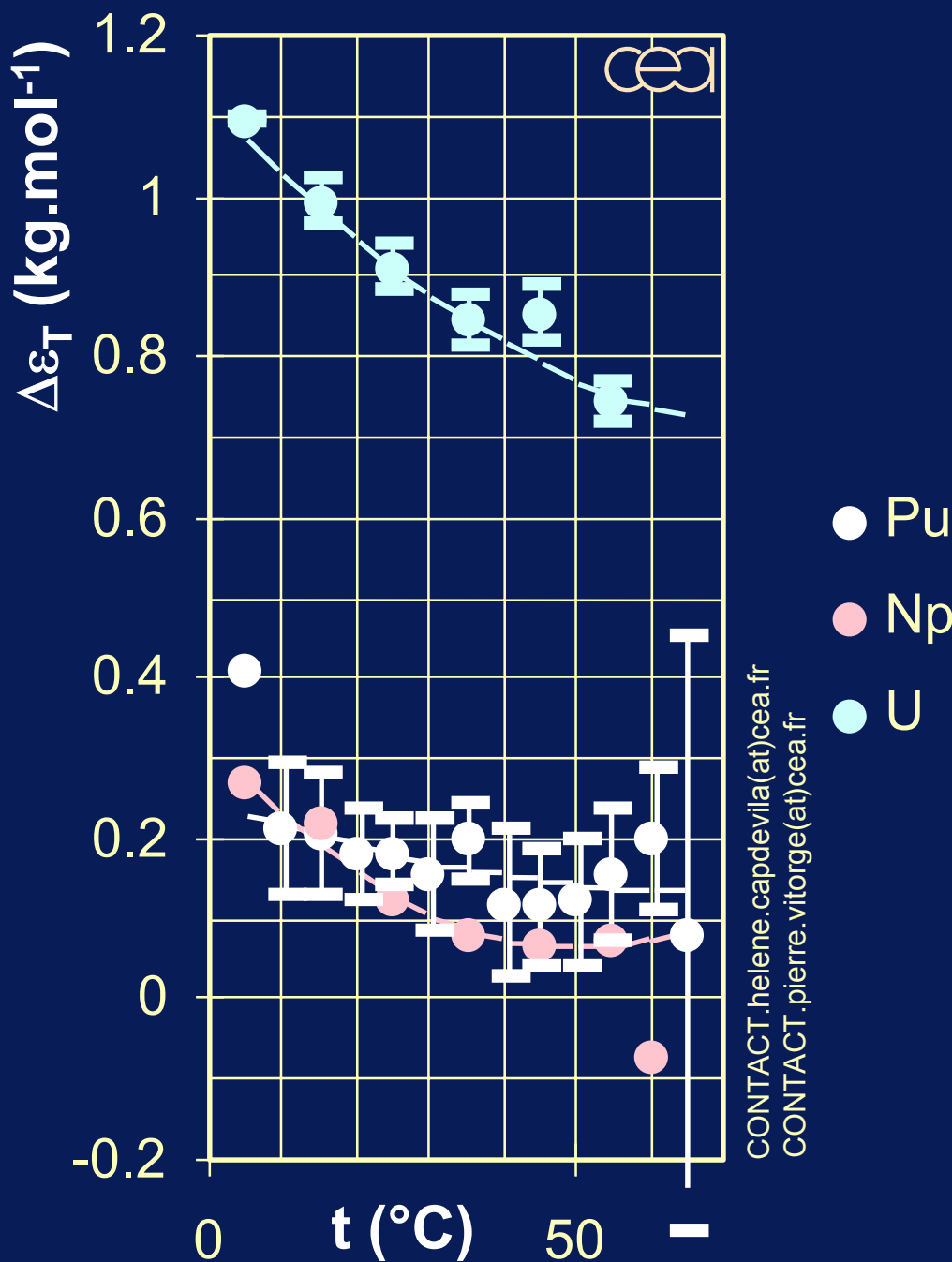
$$E_{\text{Ox/Red}(T,I)} F / (R T \ln 10) - 9 D_{T,I} = E_{\text{Ox/Red}(T,0)} F / (R T \ln 10) - \Delta \varepsilon_T m_{\text{Na}^+}$$

$$D = a_T \sqrt{I} / (1 + b_T \sqrt{I})$$

$$E_{\text{Ref}(T,I)} = E_{\text{Ag/AgCl}(T,0)} + R T [\lg m_{\text{Cl}^-} - D_{T,I} + \varepsilon_{\text{Na}^+, \text{Cl}^-(T)} m_{\text{Na}^+}] / F$$

Results: $E_{\text{Ox/Red}(T,0)}$ and $\Delta \varepsilon_T$ fitted values

Temperature Influence on SIT Coefficient



$$\Delta\varepsilon_T \approx \Delta\varepsilon_{T^\circ} + \Delta\varepsilon'_{T^\circ} \Delta T + (\Delta\varepsilon''_{T^\circ} / 2) \Delta T^2$$

$$E_{\text{Ox/Red}(T,I)} = E_{\text{Ox/Red}(T,I)}^\circ - \frac{F}{RT} \ln D_{T,I} = E_{\text{Ox/Red}(T,I)}^\circ - \frac{F}{RT} \ln \left(\frac{\Delta\varepsilon_T}{\Delta\varepsilon_{T^\circ}} m_{\text{Na}^+} \right)$$

$$\Delta\varepsilon = \varepsilon_{\text{PuO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+} - \varepsilon_{\text{PuO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+}$$

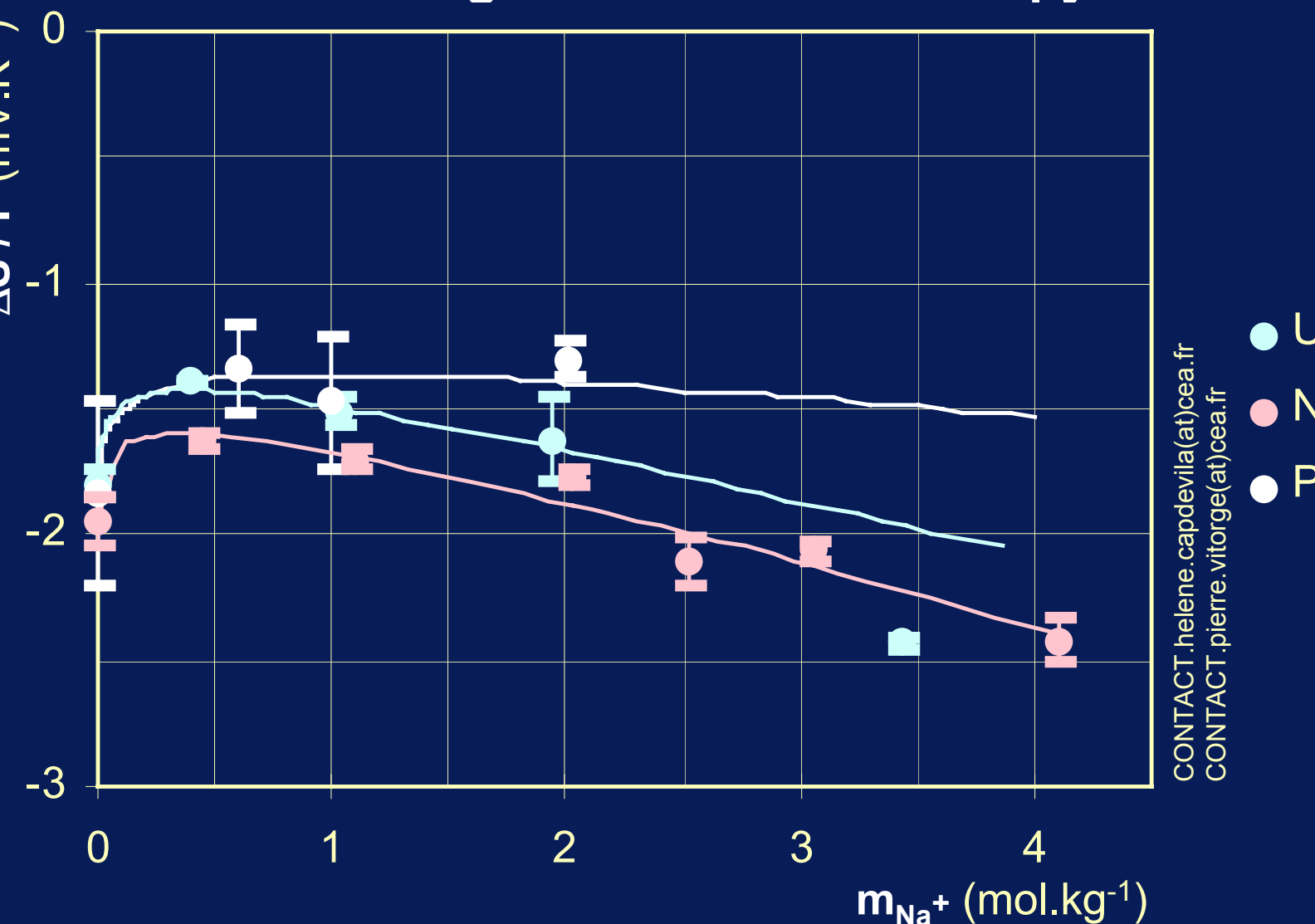
Results at T° for Pu:

$$\Delta\varepsilon_{T^\circ} = 0.18_{(0.05)} \text{ kg.mol}^{-1},$$

$$\Delta\varepsilon'_{T^\circ} = -2.1_{(0.1)} \text{ g.mol}^{-1} \cdot \text{K}^{-1},$$

$$\Delta\varepsilon''_{T^\circ} = 24 \text{ mg.mol}^{-1} \cdot \text{K}^{-2}$$

Ionic Strength Influence on Entropy



$$\Delta S_{T^\circ, I} = \Delta S_{T^\circ, 0} + [9 (D_{T^\circ, I} + T^\circ D'_{T^\circ, I}) - (\Delta \varepsilon_{T^\circ} + T^\circ \Delta \varepsilon'_{T^\circ}) m_{\text{Na}^+}] R \ln 10$$

$$E_{T, I} \approx E_{T^\circ, I} + \Delta S_{T^\circ, I} / F \Delta T + \Delta C_{p_{T^\circ, I}} / (2 F T^\circ) \Delta T^2$$

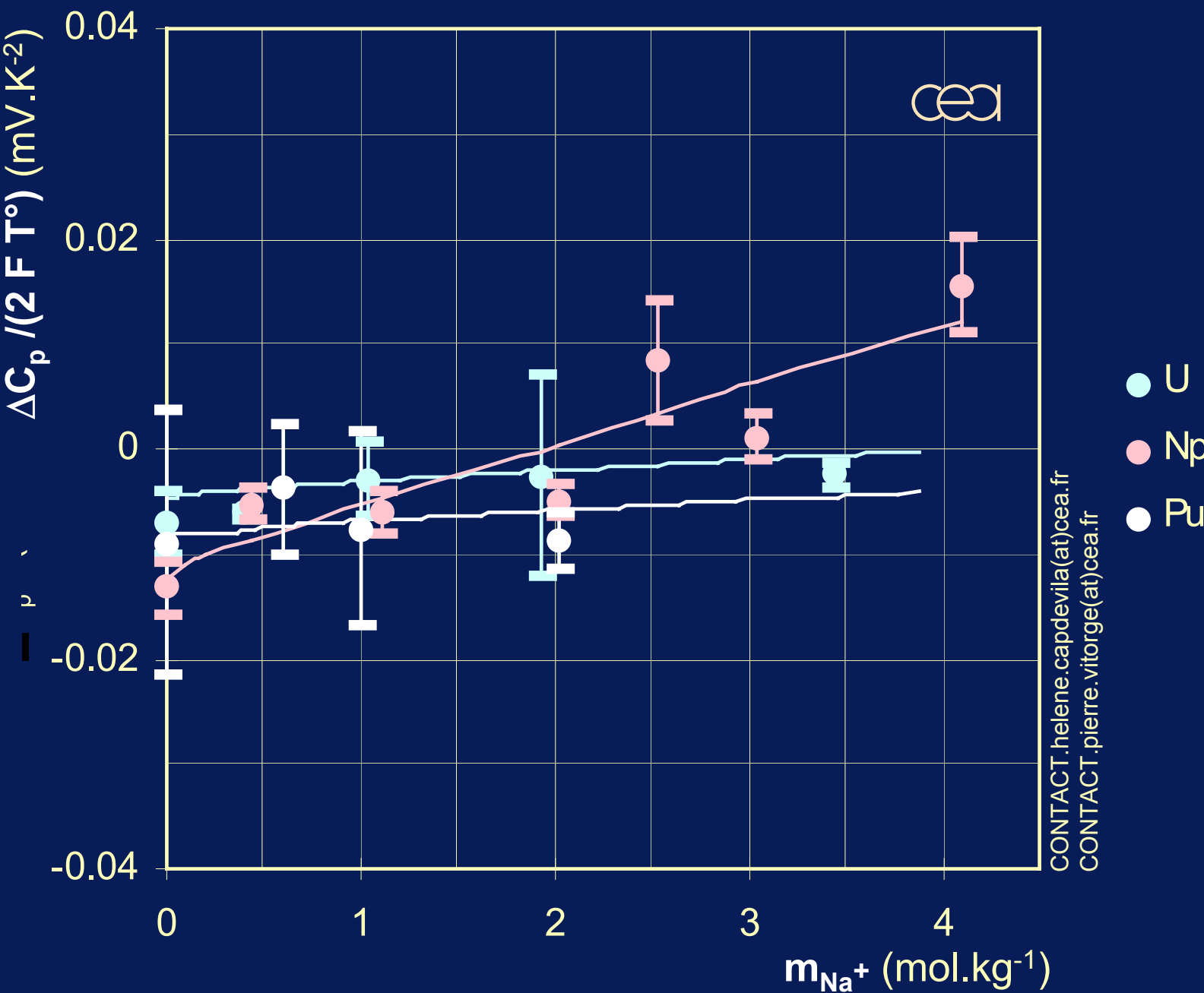
Ionic Strength Influence on Enthalpy

$$\Delta H_{T^\circ, I} = \Delta H_{T^\circ, 0} + [9 D'_{T^\circ, I} - \Delta \varepsilon'_{T^\circ} m_{\text{Na}^+}] R T^{\circ 2} \ln 10$$

$$R \ln K_{T, I} \approx R \ln K_{T^\circ, I} - \Delta H_{T^\circ, I} \Delta(1/T) + T^{\circ 2} \Delta C_{p_{T^\circ, I}} / 2 \Delta(1/T)^2$$

$$\Delta G = -R T \ln K = -F E \quad \text{or} \quad \Delta G = \Delta H - T \Delta S$$

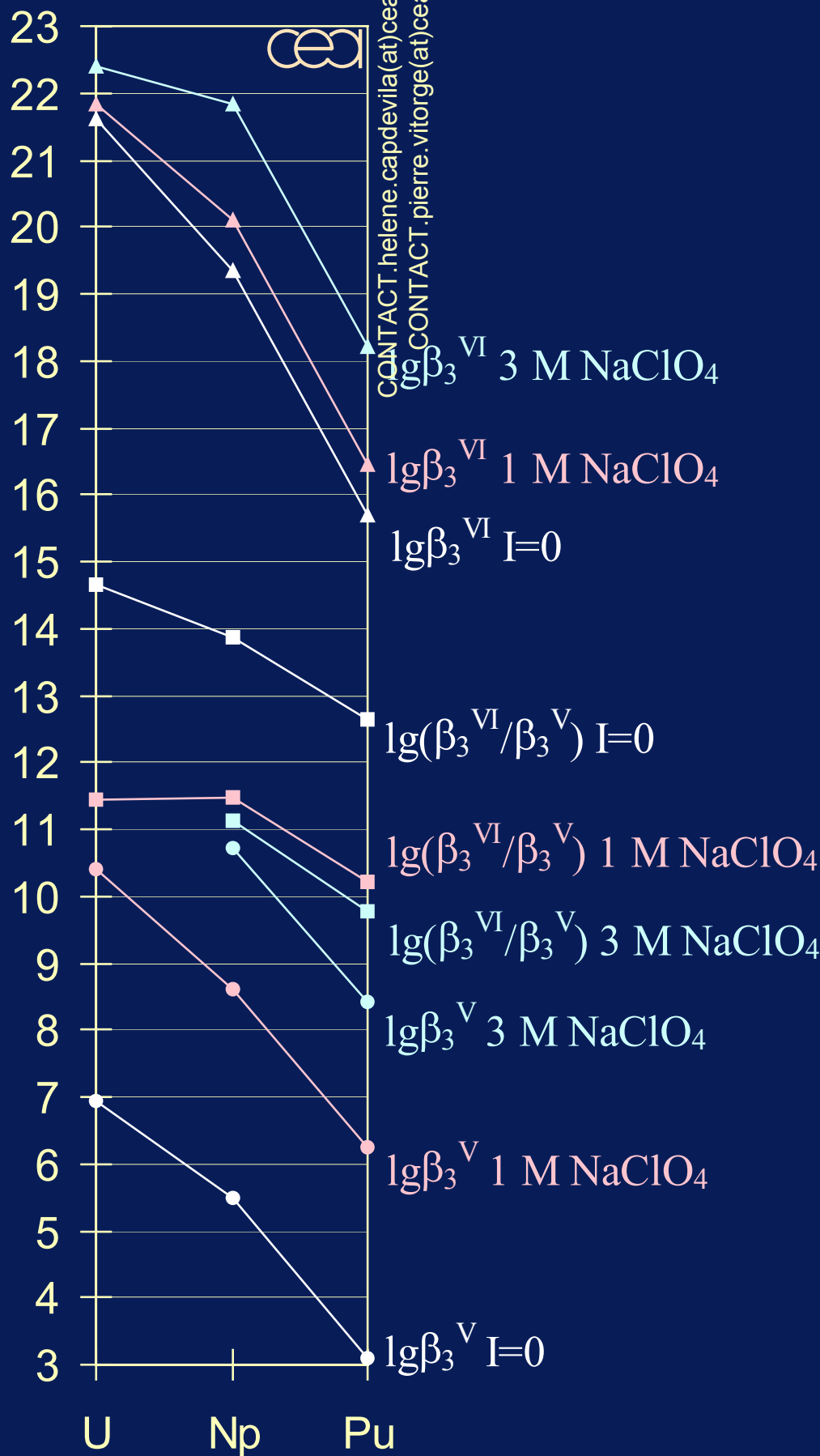
Ionic Strength Influence on Heat Capacity



$$\Delta C_{p_{T^\circ, I}} = \Delta C_{p_{T^\circ, 0}} + [9(2D'_{T^\circ, I} + T^\circ D''_{T^\circ, I}) - (2\Delta\varepsilon'_{T^\circ} + T^\circ \Delta\varepsilon''_{T^\circ})m_{\text{Na}^+}] RT^\circ \ln 10$$

$$E_{T, I} \approx E_{T^\circ, I} + \Delta S_{T^\circ, I} / F \Delta T + \Delta C_{p_{T^\circ, I}} / (2 F T^\circ) \Delta T^2$$

Formation Constants of Limiting Carbonate Complexes



$$\lg(\beta_3^V/\beta_3^{VI}) = (E_{Pu(VI)/Pu(V)} - E_{PuO_2^{2+}/PuO_2^+})F / (R T^\circ \ln 10)$$

